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FUEL CELL ELECTRODES AS STUDIED BY RUTHERFORD BACKSCATTERING

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**PLATINUM LOSS AND MIGRATION IN POROUS GAS DIFFUSION FUEL CELL
ELECTRODES AS STUDIED BY RUTHERFORD BACKSCATTERING SPECTROMETRY**

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ABSTRACT

Long-term operation of phosphoric acid fuel cell produces severe migration of the highly dispersed electrocatalyst, Pt, from the cathode to the anode. We have examined, before and after extended operation, the porous gas diffusion electrode assemblies by conventional Rutherford back-scattering spectrometry using the ion beam facility at Los Alamos. In addition, we have made computer simulations to the data that give catalyst concentration as a function of depth. The data demonstrate that after extended operation (500 to 2000 hours), Pt is lost from the cathode and is redeposited at the outermost surface layers of the anode electrode structure. This loss is significant and several factors contributing to it will be discussed.

1. INTRODUCTION

The principal electrochemical components of a phosphoric acid fuel cell (PAFC) are two parallel porous gas diffusion electrode structures, one being the anode at which hydrogen gas is oxidized to solvated protons and the other being the cathode at which oxygen is reduced to water. Electrochemical power is available by connecting a current load between the two electrodes. The electrocatalytic material for both reactions is usually highly dispersed Pt (particle sizes 20 to 50 Å) supported on porous carbon. A schematic of a single-cell PAFC component is shown in Fig. 1. Many detailed references [1-3] are available that discuss the electrochemical, materials science and systems engineering aspects of these devices. In this study we specifically address the direct loss (and migration) of Pt from the electrocatalytic cathode layer due to electrodisolution and/or corrosion. These losses have a direct bearing on the practical operating lifetime and performance of the PAFC.

The porous gas diffusion electrode is particularly amenable to analysis by Rutherford backscattering spectrometry (RBS) since we are analyzing a high Z material, Pt, in a low Z matrix containing C, O, Si (from SiC in the matrix), and P (from H_3PO_4). We have conducted pre- and post-mortem analysis on electrode assemblies containing (i) Pt at both the anode and cathode, and (ii) Pd at the anode and Pt at the cathode. The latter experimental arrangement allows us to unequivocally demonstrate and analyze for migration of Pt through the cell due to the quite different Z values of the respective elements.

II. EXPERIMENTAL

Rutherford backscattering spectroscopy (RBS) experiments were performed at the ion beam facility of the Los Alamos National Laboratory. The spectra were taken with a 2.3 (and occasionally 2.5) MeV alpha particle beam impinging at normal incidence to the electrode surface. This energy was measured at a backscattered angle of 160° with a solid-state detector. The energy resolution of the detector together with necessary electronic components was 17 to 20 keV full width at half maximum. The beam spot was typically 20 to 30 mm², and the data were collected until a preset charge (integrated current) on the sample of $\sim 2 \times 10^{-4}$ C was achieved.

The data were simulated with computer algorithms for synthesis of RBS spectra [4]. A key assumption in the computer code is that the samples are made up of a finite number of layers of different thicknesses, each with uniform composition. Further details regarding the program are contained in Ref. 4.

The depth of penetration can be estimated from Ziegler's penetration ranges for He⁺ [5]. For bulk carbon (graphite) the penetration range (R) of 2.3 MeV alphas is $7 \pm 0.2 \mu\text{m}$. Because there are backscattered particles, the depth of penetration is roughly half that of the implanted or $R = 3.4 \pm 0.2 \mu\text{m}$. Since the electrodes are mostly porous graphite, rather than bulk, the penetration range is higher. As a first approximation, we assume that the penetration is a linear function of the decrease in density (Eq. 1).

$$R_{(\text{porous})} \sim \frac{\text{Density of Bulk C}}{\text{Density of Porous C}} \times R_{(\text{bulk})} \quad (1)$$

The density of the electrodes was measured to be $\sim 0.7 \text{ gm/cm}^{-3}$, and bulk graphite density is 2.27 gm/cm^{-3} . Thus, the range increases to $\sim 11.3 \mu\text{m}$. Since the electrodes contain other materials that are heavier than carbon (O, F, Si, P, Pd, and Pt), the true penetration range is somewhat smaller. The depth of penetration can also be determined from the spectra itself. The simulations show that the number of atoms encountered by the penetrating alpha particles is $\sim 3 \times 10^{19} \text{ atoms/cm}^2$. The mass density of electrodes is 0.7 gm/cm^{-3} ; thus the range can also be calculated by Eq. (2) and found to be $\sim 8.5 \mu\text{m}$.

$$R = \frac{\frac{12 \text{ gm}}{6.02 \times 10^{23} \text{ Atoms}} \cdot 3 \times 10^{19} \frac{\text{Atoms}}{\text{cm}^2}}{0.7 \frac{\text{gm}}{\text{cm}^3}} = 8.5 \mu\text{m} \quad (2)$$

Electrochemical testing and operation of the PAFC single cells were conducted using a conventional design and apparatus [2]. The cells were run on pure H₂ and O₂ at $200 \pm 5^\circ \text{C}$. The supported Pt electrodes were of bilayer construction on carbon paper ($\sim 1 \text{ mm}$ thick)*. The outer electrocatalytic

* Electrodes were supplied by Energy Research Corporation, 3 Great Pasture Road, Danbury, CT.

layer (~100 μm thick) contained a nominal Pt loading of 0.35 mg/cm^2 . The supported Pd electrodes were of bilayer construction on carbon cloth.** The outer electrocatalytic layer contained a nominal Pd loading of 0.35 mg/cm^2 . The post-mortem electrode assemblies were washed briefly in water to remove H_3PO_4 and were ultrasonically agitated in acetone to remove the SiC matrix. Some small residual SiC and H_3PO_4 did remain on and in the electrode assembly and is readily apparent in some of the RBS data.

III. RESULTS

In Fig. 2 the RBS spectra of the unused fuel cell anode (Pd loaded onto a carbon support) and cathode (Pt loaded onto a carbon support) components are shown. The solid lines correspond to computer simulation of the data using a multilayer model. In the spectra for the unused anode, one observes edges due to C from support, O from spurious surface oxidation of the support and/or incorporation of water, F from the teflon added as wet proofing and Pd from the electrocatalyst loading. Note also, that the Pd edge displays a very prominent rounding. This is partly due to the very rough nature of the actual electrode surface (with morphological variation in the actual outer most surface position on the order of several microns) and also due to inhomogeneous distribution of the electrocatalyst. For the Pt-loaded electrode (cathode), the actual electrode surface region was morphologically smoother and the loading is more evidently uniform and in the RBS spectra and simulation. Despite this shortcoming and the limited depth into which we are penetrating, useful information on the corrosion and cross cell migration of Pt in the fuel cell device can be convincingly demonstrated. In addition, the measured Pt loading, when extrapolated to a layer thickness of $\sim 100 \mu\text{m}$, is of the same order of magnitude as the stated nominal loading of 0.35 mg cm^{-2} .

Single cell assemblies containing Pd as the active anode electrocatalyst and Pt as the active cathode electrocatalyst were run at a variety of load conditions and for various operating times. After long-term operation (500 to 2000 hours) the electrode assemblies were then disassembled and

** Electrodes were supplied by Prototech Corporation, 70 Jaconnet Street, Newton Highlands, MA.

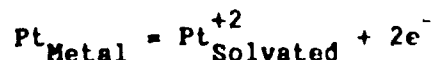
analyzed by RBS. In Fig. 3 RBS data are shown for an electrode assembly run for ~ 2000 hours under a constant initial load of 15 mA/cm^2 at a cell potential of $+0.750 \pm 0.01 \text{ V}$. Several general observations are apparent from inspection of Fig. 3. The major observation is the significant appearance of Pt now appearing at the anode structure. Solvated platinum is electrochemically deposited at the anode due to its favorable potential. In addition, the concentration of electrocatalyst component at both the anode and cathode (not shown) structures has also decreased significantly (compare the Pd to C edge/height ratio in Fig. 2 to that in Fig. 3). Other elements appear in the RBS spectra in addition to those seen in the unused electrocatalyst RBS data (Fig. 2). Phosphorous and silicon arise from incomplete removal of H_3PO_4 electrolyte and SiC in the matrix material. The Pt and Pd concentrations within the anode electrode structure are also seen to be strongly peaked with the highest concentrations at the surface.

In addition to the electrode assembly examined in Fig. 3, we have run several other single cells using the same electrode configuration operated under different load and overall cell potential conditions. For electrodes run at an overall cell potentials of $+0.650 \text{ V}$ and $+0.500 \text{ V}$ (500 hours operation at 200°C), the RBS data (not shown) also demonstrate noticeable losses of Pt from the cathode and redeposition onto the outermost surfaces of the anode. In general, we have found these losses to be variable with respect to the overall cell potential (load drawn) although always more severe for cells operated for longer periods of time.

IV. DISCUSSION

For the PAFC, the loss of activity as a function of operation time can be correlated with many factors that act either singly or in concert [6]. Flooding of the electrodes (leading to poor mass transfer of the reactant gases), loss of active Pt area as a result of sintering and corrosion, and loss of electronic conductivity caused by support corrosion, are all principal factors leading to PAFC activity losses. The results described above pertain directly to the corrosion of Pt, diffusion through the matrix, and deposition at the anode in the PAFC device.

The corrosion of bulk Pt has been studied by Bindra, Clouser, and Yeager at 200°C in 96% H_3PO_4 and found to be Nernstian [7] corresponding to the proposed electrochemical corrosion reaction:



Their results demonstrated that Pt solubility at 0.75 V (versus a reversible hydrogen electrode) can be estimated to be ca. 10^{-8} M. The equilibrium solubility increased dramatically with potential and rather large equilibrium solubility values ($\sim 10^{-4}$ M) are obtainable at potential values near open circuit ($\sim +0.95$ V).

A rather simple flux equation, given by Eq. 3, can be used [8] to estimate the net rate of Pt loss from the cathode and redeposition at the anode. Here N represents the rate of this process,

$$N \approx \frac{DC^0}{l}, \quad (3)$$

in which D is the average diffusion coefficient of all solvated Pt species, C^0 is the equilibrium solubility of all solvated Pt species, and l is the interelectrode distance shown in Fig. 1. For $D = 10^{-5} \text{ cm s}^{-1}$, $C^0 \approx 10^{-8} \text{ M}$ (@ 0.75 V), and $l = 0.1 \text{ cm}$, N corresponds to $7.2 \times 10^{-10} \text{ g Pt} \cdot \text{cm}^{-2} \text{ Hr}^{-1}$ (@ 0.75 V). The RBS hr^{-1} results of Fig. 3 allow us to measure directly the concentration of Pt migrating through the single cells. The total Pt crossover concentration contained in Fig. 3 is equivalent to $1.4 \times 10^{-6} \text{ g/cm}^2$, which is in excellent agreement with the dissolution rate, N multiplied by the operating time, 2000 hours.

The observation that similar losses of Pt occur for electrode assemblies run under sufficient load such that their operating potentials should be low enough to prevent significant dissolution is noteworthy. Given the complex nature of the porous gas diffusion electrode, one must remember that the potential experienced by all the dispersed Pt is not the same. Secondly, the potential experienced by small particles is modified by the Kelvin equation [9-10]; therefore, their dissolution rates may be considerably higher. Another aspect that contributes to the measured Pt deposited at the anode is the number of carbon particles (with Pt on them) that are not in good electronic contact

with the current-collecting electrode structure. Platinum on such particles would in effect be at open circuit and the dissolution process should proceed very rapidly at such sites. Closely related to this last idea is the corrosion occurring at the intimate interface between the highly dispersed Pt and carbon. This corrosion process has been demonstrated [11] to be significant at potentials as low as +0.6 V.

In summary, many factors undoubtedly contribute to the overall Pt dissolution (corrosion) occurring in PAFC devices. A full detailed discussion of each of these contributing factors is beyond the scope of this article. However, measuring the overall Pt dissolution, migration and redeposition in real PAFC electrode assemblies is readily accomplished using RBS.

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FIGURE CAPTIONS

- Fig. 1 Schematic diagram of a PAFC.
- Fig. 2a RBS spectrum (2.5 MeV alpha) from an unused cathode with Pt as
the electrocatalyst.
- Fig. 2b RBS spectrum (2.3 MeV alpha) from an unused anode with Pd as
the electrocatalyst.
- Fig. 3 RBS spectrum of a used anode indicating the cross cell migration
and deposition of Pt.

H₃PO₄ FUEL CELL EXPLODED VIEW - SINGLE CELL

ELECTROCHEMICAL REACTIONS

